6 The particle in a one-dimensional box

6.1 Potential and boundary conditions

Consider a particle of mass m in a one-dimensional box of length L. A potential that models the walls of a box must not allow the particle to get out of the range $0 \leq x \leq L$. One way to achieve this is with a potential that is infinite outside the box

$$V(x) = \begin{cases} 0 & \text{if} \quad 0 \leq x \leq L \\ \infty & \text{if} \quad x < 0 \text{ or } x > L. \end{cases} \tag{1}$$

A wave function that describe the particle in the box must satisfy $\psi(x) = 0$ if x is outside the box. Because the wave function must be continuous, the value of $\psi(x)$ at the walls must also be zero. It follows then that

$$\psi(0) = \psi(L) = 0. \tag{2}$$

This is an example of **boundary conditions.**[1]

[1] Boundary conditions are a set of constraints considered when solving a differential equation.

6.2 Schrödinger equation

We can now write the Schrödinger equation for the particle in a one-dimensional box. We only consider points inside the box. In this case the Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}. \tag{3}$$

Note that the potential inside the box is zero.

The Schrödinger equation is given by

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x). \tag{4}$$

This is a homogeneous second-order differential equation and its solution is known

$$\psi(x) = A\cos(kx) + B\sin(kx), \tag{5}$$

and the constants A, B, and k must be determined by imposing the boundary conditions. We can very that this is a solution to the Schrödinger equation by plugging it in

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left[A\cos(kx) + B\sin(kx)\right] = \underbrace{\frac{\hbar^2 k^2}{2m}}_{E}\left[A\cos(kx) + B\sin(kx)\right]. \tag{6}$$

We indeed see that once we apply the Hamiltonian we get back the same function times a number, which is the eigenvalue

$$E = \frac{\hbar^2 k^2}{2m} \tag{7}$$

Imposing $\psi(x = 0) = 0$ we get

$$\psi(0) = A\cos(0) + B\sin(0) = A = 0, \tag{8}$$

which implies that A must be zero. Imposing $\psi(x = L) = 0$ we get

$$\psi(L) = B\sin(kL) = 0. \tag{9}$$

Recall that $\sin(x) = 0$ if $x = n\pi$ where n is an integer $n = 0, \pm 1, \pm 2, \ldots$. It follows that $kL = n\pi$, in other words

$$k = \frac{n\pi}{L} \tag{10}$$

Notice that this condition imposes that k is quantized. Quantization is a consequence of the fact that we imposed boundary conditions on the Schrödinger equation. Now if we plug this solution in the wave function we get

$$\psi_n(x) = B \sin\left(\frac{n\pi x}{L}\right). \tag{11}$$

Note that the solution with $-n$ is equivalent because it only differs in the sign[2]

$$\psi_{-n}(x) = B \sin\left(\frac{-n\pi x}{L}\right) = -B \sin\left(\frac{n\pi x}{L}\right) = -\psi_n(x). \tag{12}$$

[2] Recall our discussion of equivalent wave functions and phase factors?

Of these two equivalent solutions we can discard those with negative integers n. Also, notice that when n we get a very sad solution

$$\psi_0(x) = B \sin\left(\frac{0\pi x}{L}\right) = 0. \tag{13}$$

As we discussed before, this is not a good solution because there is no way we can normalize it. These considerations leaves us with the following value of the quantum number n

$$n = 1, 2, 3, \ldots \tag{14}$$

Exercise 6.1 Draw the energy spectrum of the particle in the box model. ■

6.3 Energy

We can now derive an expression for the energy

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mL^2} = \frac{h^2 n^2}{8mL^2}, \quad n = 1, 2, 3 \ldots \tag{15}$$

6.4 Wave function

Next, we should check if the wave function is normalized. To do this, we compute the integral of the wave function probability density[3]

$$\int_0^L dx\, |\psi_n(x)|^2 = |B|^2 \int_0^L dx\, \sin^2\left(\frac{n\pi x}{L}\right) = |B|^2 \frac{L}{2} \tag{16}$$

[3] Here we need the integral $\int \sin(x)^2 dx = \frac{x}{2} - \frac{1}{4}\sin(2x) + C$.

This wave function is not normalized because the quantity $|B|^2 \frac{L}{2}$ is generally not equal to one. However, we can pick a value of B that makes the wave function normalized. As you can easily verify, if we set $B = \sqrt{\frac{2}{L}}$ then the wave function is normalized. We finally arrive at the normalized expression for the wave function

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right). \tag{17}$$

Exercise 6.2 Draw the first four wave functions and corresponding probability distributions for the particle in a box model. Where is the probability of finding the particle highest and the lowest? ■